



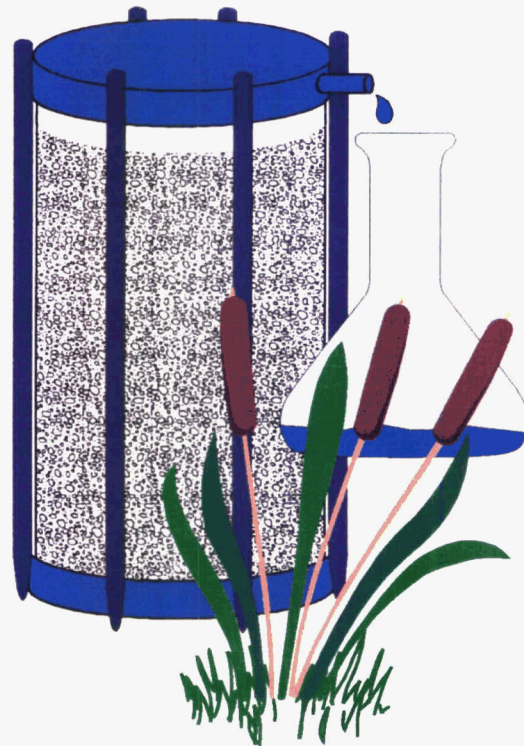
# Environmental Sciences Laboratory

## Chemical Mechanism of Uranium Uptake by Zero-Valent Iron: Results of a Column Experiment

Permeable Reactive Barrier Project  
Monticello, Utah

April 2000

Prepared by  
U.S. Department of Energy  
Albuquerque Operations Office  
Grand Junction Office  
Grand Junction, Colorado



MRAP OUIII AR 656 8-2 PERT WALL VALENT  
CHEMICAL MECHANISM OF URANIUM UPTAKE BY  
ZERO VALENT IRON RESULTS OF A COLUMN 4/00



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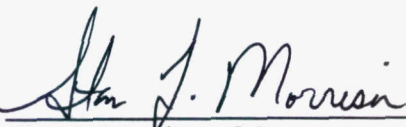
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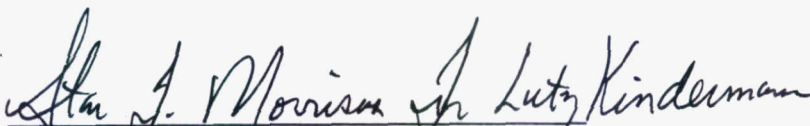
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Prepared By:



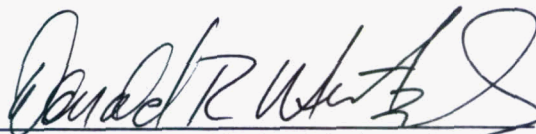
Stan J. Morrison, Manager  
Environmental Sciences Laboratory

Reviewed By:



Lutz Kindermann, Geochemist  
UMTRA Ground Water Project

Approved By:



Donald R. Metzler, Project/Technical Manager  
U.S. Department of Energy

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Appendix A	Environmental Sciences Laboratory Work Submittal
Appendix B	Environmental Sciences Laboratory Notes
Appendix C	Data Summary



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## Acronyms

AFO	amorphous ferric oxyhydroxide
ASTD	Accelerated Site Technology Deployment
cm	centimeters
DOE	U.S. Department of Energy
ESL	Environmental Sciences Laboratory
g	gram
GJO	Grand Junction Office
$\mu$ L	microliter
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mL/g	milliliters per gram
mL/min	milligrams per minute
mM	millimols
mm	millimeters
MMTS	Monticello Mill Tailings Site
mV	millivolts
nm	nanometers
ORP	oxidation reduction potential
PRB	permeable reactive barrier
U	uranium
$\mu$ g/L	micrograms per liter
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction
ZVI	zero-valent iron

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## Executive Summary

The purpose of this study is to provide data that would distinguish between two chemical mechanisms that have been proposed to explain the effect of zero-valent iron (ZVI) in removing uranium (U) from groundwater. The two mechanisms are reductive precipitation and adsorption on ZVI corrosion products. A column experiment was conducted under conditions designed to limit the formation of ferric oxides or oxyhydroxides and to limit adsorption of U to these corrosion products.

A total volume of 70.7 liters (5,400 pore volumes) of solution containing  $\text{NaHCO}_3$ , sodium azide (a bactericide), and U was passed through a column containing ZVI. Uranium concentrations decreased from 2,000 to less than 88 micrograms per liter ( $\mu\text{g/L}$ ) for the first 3,000 pore volumes and were less than 10  $\mu\text{g/L}$  for the first 700 pore volumes. After 3,000 pore volumes, the U concentration began a steady rise and exceeded 1,000  $\mu\text{g/L}$  at 5,437 pore volumes.

Adsorption to corrosion products accounted for only 0.5 percent of the 76 milligrams of U that were removed from the solution passing through the column. The results indicate that adsorption to Fe (III) oxide and oxyhydroxide corrosion products is relatively insignificant in removing U from a solution in contact with ZVI. The results, however, are consistent with U removal by reductive precipitation. The reaction rate is relatively fast, removing nearly all U within 6.5 minutes of contact with ZVI.

After 3,000 pore volumes, U removal became less efficient despite the presence of an abundance of ZVI. When the column flow rate was slowed from 2 milliliters per minute to 0.2 milliliter per minute, the U concentration in the effluent decreased from 1,055 to 129  $\mu\text{g/L}$ , indicating that ZVI was still capable of removing U but at a diminished rate. Possibly, corrosion caused a reaction rim with mineral deposits such as magnetite that increased the distance required for diffusion processes to bring U into contact with ZVI.

Results of x-ray diffraction analysis show that ZVI was the major solid phase remaining after the experiment. A small percentage of magnetite was formed by corrosion. A small amount of manganese was leached from the ZVI. Uranium concentration in the original (unused) ZVI was 8.6 milligrams per kilogram ( $\text{mg/kg}$ ) and ranged from 778 to 3,400  $\text{mg/kg}$  in effluent samples of the column experiment.



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## 1.0 Introduction

The purpose of this study is to provide data that would distinguish between two chemical mechanisms that have been proposed to explain the effect of zero-valent iron (ZVI) in removing uranium (U) from groundwater. The two mechanisms are reductive precipitation and adsorption on ZVI corrosion products.

The work described in this report is a portion of a larger project, the Monticello Permeable Reactive Barrier (PRB) project, that is funded by the Accelerated Technology Deployment (ASTD) Program sponsored by the U.S. Department of Energy (DOE) Office of Science and Technology. The PRB project is being conducted by four teaming partners: the DOE Grand Junction Office (GJO), Sandia National Laboratories/New Mexico, DOE Western Environmental Technology Office (MSE Technology Applications, Inc.), and the University of Waterloo, Ontario, Canada.

The Monticello PRB project designed and installed a PRB to treat U-contaminated groundwater at the Monticello Mill Tailings Site (MMTS) in summer 1999 (DOE 1999a). The MMTS is located near the city of Monticello in southeastern Utah. A uranium and vanadium processing mill was operated at the site from mid-1940 until 1960. The MMTS was placed on the National Priorities List in 1989 and is being remediated in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act. DOE, the U.S. Environmental Protection Agency (EPA), and the State of Utah entered into a Federal Facilities Agreement that specifies DOE as the lead agency and gives oversight authority to EPA and the State of Utah. During 1998 and 1999, tailings and tailings-contaminated soils and other materials were relocated to a disposal site approximately 2 miles south of the millsite. The PRB was designed to treat residual groundwater contamination and was included as part of an interim record of decision for the MMTS. Contaminated groundwater flows through a shallow alluvial aquifer that is underlain by impermeable bedrock. Contaminants of concern include arsenic, lead-210, manganese, selenium, uranium, and vanadium.

Laboratory work was conducted in the Environmental Sciences Laboratory (ESL) at the GJO from January 11 through 17, 2000. Appendix A contains the ESL work submittal, Appendix B contains copies of the ESL laboratory notes, and Appendix C contains the calculations.

The ESL was established in 1991 to provide support to programs at the GJO. The 4,500-square-foot geochemical laboratory is equipped with bench space and equipment to conduct research, treatability studies, and pilot-scale tests to supplement numerical modeling and to evaluate promising remediation technologies. The ESL also maintains an ecology laboratory equipped to conduct testing to design and evaluate landfill covers and phytoremediation technologies and operates a mobile laboratory that is routinely used for expedited site characterization at field sites.

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## 2.0 Background on Chemical Mechanisms for ZVI-Based Permeable Reactive Barriers

A PRB is an engineered zone of reactive material that treats contaminated groundwater flowing through it. PRBs have been constructed of several reactive materials, including ferric oxyhydroxide, phosphate, granular activated carbon, zeolite, and ZVI, but ZVI is the most commonly used material.

In addition to the MMTS, PRBs are being used to treat U-contaminated groundwater at sites at Fry Canyon, Utah; Durango, Colorado; and the DOE Oak Ridge National Laboratory. Contact with ZVI causes U concentrations to decrease to a few micrograms per liter ( $\mu\text{g/L}$ ) at all four sites. Results of numerous laboratory experiments have confirmed the ability of ZVI to remove U from groundwater. Because of the promising results of laboratory and field studies, there is an increasing interest throughout the DOE system to use ZVI to treat U-contaminated groundwater. Research is still needed, however, to understand the mechanisms of U uptake to support optimal designs for remediation systems.

Two fundamentally different reactive mechanisms have been proposed to explain the uptake of U by ZVI (Cantrell et al. 1995). In one proposed mechanism, ZVI causes the oxidation state to decrease, resulting in reduction of U(VI) to U(IV) (Reaction 1). Uranium(IV) is transferred from the aqueous phase to low-solubility minerals such as uraninite ( $\text{UO}_2 \cdot x\text{H}_2\text{O}$ ). In the other mechanism, ferric oxyhydroxides or oxides are formed as ZVI is oxidized by groundwater. The ferric oxyhydroxides subsequently adsorb the dissolved U(VI). Cantrell et al. (1995) suggested that reductive precipitation is dominant and demonstrated its feasibility by using thermodynamic calculations.



Fieder et al. (1998) conducted experiments with a small disk (0.55 inch [in.] diameter by 0.063 in. thick) of mild steel immersed in 300 milliliters (mL) of aqueous solution, and concluded that the dominant mechanism for U removal by ZVI is by adsorption on ferric oxyhydroxide corrosion products. When the experiments were conducted under aerobic conditions, U sorbed rapidly to the ferric oxyhydroxides, but U was slowly and incompletely reduced under anaerobic conditions. The surfaces of the solid phases in the aerobic experiments contained only uranyl, whereas the surfaces of the solid phases in the anaerobic conditions contained about 75 percent uranous as determined by x-ray photoelectron spectroscopy (XPS). Fiedor et al (1998) deduced that some reductive precipitation occurred but the reaction was too slow to account for the observed rate of U removal in the experiments. They also indicated that reductive precipitation would not contribute significantly to U uptake in a PRB containing ZVI.

In contrast, Gu et al. (1998) provided experimental data confirming that reductive precipitation caused by ZVI is the dominant U uptake mechanism. The experiments consisted of agitating 2 grams (g) of granular ZVI with 10 milliliters (mL) of a solution containing 42 millimols (mMol) (10,000 mg/L) of U for 3 weeks. The reaction products were separated from the ZVI by decanting and filtering. Less than 4 percent of the U was associated with the suspended reaction products. A solution of 0.1 M  $\text{Na}_2\text{CO}_3$  solution readily removed U from reaction products but not from residual ZVI, signifying that U was adsorbed to reaction products but not to ZVI.



Fluorescence spectroscopy confirmed that the U on the surfaces of the ZVI was in the IV oxidation state, whereas U associated with suspended reaction products was in the VI oxidation state. Gu et al. (1998) demonstrated that the rate of U uptake in the presence of ZVI was slower than adsorption rates and that the shape of sorption isotherms indicated precipitation rather than adsorption, further evidence supporting a mechanism of reductive precipitation.

### 3.0 Methods

The experiment was conducted in a glass column with an inside diameter of 15 millimeters (mm) containing 37 g of -8 +18 mesh ZVI supplied by Peerless Metal Powders & Abrasive, Detroit, Michigan (Figure 1). The column was lightly tamped while filling; the flow length through the ZVI was 120 mm. The column was purged overnight with argon before starting the experiment. Influent solution was stored in a plastic tank and was constantly purged of oxygen by bubbling the solution with high-purity argon (Figure 2). Argon escaped through a 3-millimeter (mm) hole in the cap. All joints were wrapped with wax film to minimize exposure to air; Tygon tubing was used for connections (Figure 1). Effluent was collected in a plastic tank and was also purged constantly with argon (Figure 2). Effluent samples were analyzed under argon immediately after collection for pH, dissolved oxygen (DO), and oxidation reduction potential (ORP). Alkalinity and conductivity were measured within an hour of collection, and samples were preserved with  $\text{HNO}_3$  for Fe and U analyses. On the basis of the amount of solution required to fill the column, 1 pore volume is equivalent to 13 mL. A peristaltic pump was used to pump the solution through the column at 2 milliliters per minute (mL/min), resulting in a residence time of 6.5 minutes.

The influent solution was made by the addition of reagent grade chemicals to milli-Q pure water. The composition was 1,638 mg/L  $\text{NaHCO}_3$ , 100 mg/L of sodium azide (a bactericide), and 200 microliters per liter ( $\mu\text{L/L}$ ) of a 10,000-mg/L U solution containing 3 percent  $\text{HNO}_3$ . The pH of the solution was adjusted to 9.2 with the addition of about 60  $\mu\text{L}$  of 10N NaOH. Alkalinity of the solution was about 950 mg/L (as  $\text{CaCO}_3$ ).

After completing the flow portion of the experiment, ZVI was dried by passing argon through the column for 2 days. After the column material was completely dry, the column was opened and six samples of 20 mm of the column material were collected; an additional sample of original ZVI was also sampled. Each of the seven samples was split into three portions. One portion of each sample set was embedded in epoxy and made into a polished thin section, one portion was digested for chemical analysis, and one portion was used for x-ray diffraction (XRD) analysis.

The sample for XRD analysis was powdered in an agate mortar, placed in a randomly oriented mount, and analyzed using Cu  $K\alpha$  radiation at 40 millamps and a scan speed of  $1^\circ 2\theta$  per minute. XRD is a semiquantitative technique that usually requires the presence of more than 1 percent of a mineral to make an identification. The intensity of the magnetite peak was calibrated using magnetite standards that provided accuracy of about  $\pm 3$  percent.

Because ZVI is difficult to digest, two different processes were used: (1) a mixture of hot concentrated nitric, hydrofluoric, and perchloric acids and (2) microwave digestion with concentrated nitric acid (EPA 1994). A small residual remained after digesting with the first method and a slightly larger residual remained with the second method. The digestate solutions interfered slightly with the analysis of Fe with the first digestion method and the analysis of U with the second digestion method. The concentrations measured of both digestions were similar; data derived from the first digestion method were used because a larger proportion of the sample was digested.



Values of pH were determined using a silver/silver chloride glass combination electrode calibrated daily using pH buffer solutions at the same temperature as the solutions being measured (ESL procedure AP[pH-1], DOE 1999b). Values of ORP were determined using a platinum redox and a silver/silver chloride reference combination electrode (ESL procedure AP[ORP-1], DOE 1999b). ORP of a standard ZoBell solution was measured daily and Eh values were computed by adding 200 millivolts (mV) (difference between ORP measured on ZoBell solution and the potential of ZoBell solution relative to the standard hydrogen electrode) to the ORP values. DO was measured using the semipermeable membrane method with a YSI Model 55 probe (ESL procedure AP[DO-1], DOE 1999b). Calibration was performed using water equilibrated with atmospheric oxygen. A zero oxygen check with a solution of 1 g sodium sulfite and 1 milligram (mg) cobalt chloride indicated that the lower detection limit was about 0.1 mg/L of O<sub>2</sub>. Conductivity measurements were made with a conductivity probe calibrated using 1,000 and 10,000 microsiemens per centimeter (μS/cm) standards. Alkalinity was measured by titration with H<sub>2</sub>SO<sub>4</sub> (ESL procedure AP[Alk-1], DOE 1999b). Iron and Mn concentrations in the digested samples were determined by inductively coupled plasma (ICP) atomic emission spectrometry and the U concentration was measured with ICP mass spectrometry.

Dissolved Fe concentration was measured with flame atomic absorption spectrometry (ESL procedure AP[Fe-1], DOE 1999b). Dissolved U concentration was measured with laser-induced kinetic phosphorescence analysis on a Chemcheck KPA-11 analyzer (ESL procedure AP[U-2], DOE 1999b). This method only responds to U(VI), but samples oxidized with nitric acid and peroxide provided equivalent readings, indicating that all dissolved U was in the +VI oxidation state. The Chemcheck KPA-11 method was able to detect concentrations of U less than 0.1 μg/L.

## 4.0 Results

A total volume of 70.7 liters (5,400 pore volumes) of solution was passed through the column. Uranium concentrations decreased from 2,000 to less than 88  $\mu\text{g/L}$  for the first 3,000 pore volumes and were less than 10  $\mu\text{g/L}$  for the first 700 pore volumes (Figure 3). After 3,000 pore volumes, the U concentration steadily increased and exceeded 1,000  $\mu\text{g/L}$  at 5,437 pore volumes. At that time, flow was reduced from 2 to 0.2 mL/min for 15 hours. The U concentration in the last sample, collected at the lower flow rate, decreased to 129.4  $\mu\text{g/L}$ , indicating that the uptake capacity of the ZVI had not yet been depleted (Figure 3).

Values of pH in the effluent were nearly the same as in the influent and ranged from 9.04 to 9.68 (Figure 4). Alkalinity in the effluent was only slightly lower (about 4 percent) than in the influent for most samples (Figure 5). Conductivity values were nearly the same in the effluent as in the influent (Figure 6). Influent concentrations of Fe were always less than the detection limit of 0.1 mg/L (Figure 7). Effluent concentrations of Fe were as high as 1.66 mg/L during the early portion of the experiment but decreased to less than the detection limit of 0.1 mg/L after 3,000 pore volumes. Dissolved oxygen concentrations averaged about 0.3, only slightly above the detection limit of 0.1 mg/L, in the influents and the effluents (Figure 8). Values of Eh were similar in influent and effluent, ranging from about 300 to 400 millivolts (mV) (Figure 9).

The only visible alterations in the column were slight reddish to grayish green coloration in the bottom 1 centimeter (cm) of ZVI and a few small (1- to 2-mm diameter) patches of greenish material in the top 1 cm of ZVI. Observations with a binocular microscope of ZVI samples removed from the column indicated that the grains retained their curl and lath shapes, but the surfaces appeared dull and gray compared with the shiny black surfaces of the original ZVI. Observations using reflected light at high power on polished thin sections showed that the ZVI grains were unaltered except for a thin (less than 10 micrometers) surface coating.

Results of x-ray diffraction analysis showed that ZVI was the major solid phase remaining after the experiment (Table 1). The original ZVI sample contained about 3 percent magnetite, while the column samples had 3 to 10 percent magnetite. Trace amounts of quartz that were present were likely contaminants from the intense grinding in the agate mortar. Traces of pyrite were observed in both the original ZVI and the column samples. Traces of hematite in four column samples and a questionable trace of siderite in one column sample were also noted.

Fe concentrations in the column solids ranged from 84.2 to 85.9 percent, similar to the original ZVI that had 85.0 percent Fe (Table 2). The Mn concentration in the original ZVI sample (5,980 milligrams per kilogram [mg/kg]) was higher than the column samples that ranged from 4,590 to 5,620 mg/kg. A small amount of Mn had probably leached from the original material. Uranium concentration in the original ZVI was 8.6 mg/kg; U concentrations ranged from 778 to 3,400 mg/kg in the samples of ZVI in the column (Table 2). The mass of U in the column material calculated from the concentration in the solids was 76 percent of the mass calculated from the decrease in concentrations in the solution. The difference is probably due primarily to the inhomogeneity of the solid samples.



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## 5.0 Discussion

The column experiment was conducted under anaerobic conditions designed to limit the formation of Fe(III) oxyhydroxides. From microscopic examination, the determination was made that probably less than 1 percent of the Fe was oxidized to Fe(III) oxides or oxyhydroxides. The solution composition (high pH and high dissolved carbon) was chosen to limit the amount of U adsorption, even if some Fe(III) oxyhydroxides formed. Amorphous ferric oxyhydroxide (AFO) is the most adsorbent form of Fe(III) for U (Hsi and Langmuir 1985). If 1 percent of the ZVI in the column (0.37 g [0.0066 mol] Fe) was converted to AFO, 0.00066 mol of sites (based on 0.1 mol site per mol Fe [Morrison et al. 1995]) would be available for adsorption. For the influent solution conditions, the maximum adsorption density on AFO is 0.001 mol U per mol adsorption sites (Morrison et al. 1995). Therefore, the maximum amount of U adsorbed to AFO in the column is  $6.6 \times 10^{-7}$  mol (0.16 mg) and can account for only 0.2 percent of the 76 mg of U that was removed from the solution passing through the column. Even if all the ZVI were converted to AFO, only 15.7 mg or 21 percent of the U could be adsorbed.

Magnetite ( $\text{Fe}_3\text{O}_4$ ) was identified in all ZVI samples, including the original ZVI sample (Table 2). Up to 10 percent of the column samples was magnetite that had formed from corrosion of the ZVI. Adsorption to magnetite could account for additional uptake of U from the solution. Distribution ratios (ratio of the concentration of a trace constituent on a solid phase to the concentration in the liquid phase) for U on magnetite have been measured at 4 milliliters per gram (mL/g) (Morrison and Spangler 1992) and 20 mL/g (Bostick et al. 1996; Farrell et al. 1999). Using the highest distribution ratio (20 mL/g) and assuming 10 percent magnetite (about 5 g), adsorption to magnetite can only account for 0.20 mg of U or about 0.3 percent of the 76 mg of U that was removed.

These results indicate that adsorption to Fe(III) oxides and oxyhydroxides is relatively insignificant in removing U from a solution contacting ZVI. The results, however, are consistent with U removal by reductive precipitation. Reduction of U caused by oxidation of ZVI would result in the removal of U as long as ZVI is present and accounts for the high amount of U removal that was not explained by adsorption.

While reductive precipitation is consistent with the results of the laboratory column experiment, no identifications of specific uranous minerals were made in this study or have been identified in other studies of U uptake by ZVI. It is widely assumed that the process involves precipitation of a common uranous oxide such as uraninite ( $\text{UO}_{2+x}$ ). Uraninite is the most common ore mineral found in ore deposits that were formed at low temperature (about 25 °C), with coffinite ( $\text{USiO}_4 \cdot n\text{H}_2\text{O}$ ) and brannerite  $[(\text{U}, \text{Ca}, \text{Y}, \text{Ce})(\text{Ti}, \text{Fe})_2\text{O}_6]$  often of secondary importance. While the U in uraninite is mostly reduced, uraninite always contains some uranyl component and can consist of as much as 75 percent uranyl (Finch and Murakami 1999).

Although U minerals have not been identified in any ZVI samples, Fiedor et al. (1998) used XPS to determine that more than 75 percent of the U deposited on the surface (less than 10 nanometers [nm] thick) of a steel disk under anaerobic conditions was U(IV); Gu et al. (1998) determined that U deposited with granular ZVI in a laboratory experiment was reduced to U(IV). Both Fiedor et al. (1998) and Gu et al. (1998) also identified U(VI) associated with fine-grained oxidized materials. Matheson and Goldberg (1999) used XPS to detect a mixture of U(IV) and



U(VI) associated with ZVI samples collected from two PRBs. Most of the U(VI) observed in these studies was probably adsorbed on AFO and other fine-grained ferric corrosion products, but the original deposition of U could have been from reductive precipitation. Some U(VI) may have resulted from oxidation after sampling but before analysis, especially since XPS only examines the outer 10 nm of the surface.

The Eh value (average about 350 mV) in the column effluents was much higher than in effluents from column experiments in other studies and in effluent from field PRBs. The residence time in this column (6.5 min) was significantly shorter than in most other studies. The Eh values of the column effluents were similar to the influent Eh values, indicating that reaction with ZVI has not significantly affected the chemistry of the bulk fluid. Electron transfer near the ZVI surface in conjunction with the high flow rate of solution through the pores could have established a sharp chemical gradient with little change to bulk fluid chemistry. Under these assumptions, U removal rate is diffusion controlled.

After 3,000 pore volumes, U removal was less efficient despite the abundance of ZVI still present (Figure 3). However, when the column flow rate was slowed from 2 to 0.2 mL/min, the U concentration in the effluent decreased from 1,055 to 129  $\mu\text{g/L}$  (last two points on Figure 3), indicating that ZVI was still capable of removing U but at a diminished rate. Possibly, corrosion causes a reaction rim with mineral deposits (such as ferrous hydroxide or magnetite) that increases the distance required for diffusion processes to bring U into contact with ZVI. As the reaction rims grow, the U removal rate may continue to decrease.

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Table 1. Results of X-Ray Diffraction Analysis (weight percent)<sup>a</sup>

Sample Number	Quartz	Siderite	Pyrite	Magnetite	Hematite	ZVI
S0 (original)			tr	3		MM
S1 (bottom)	tr	tr?	1	10	tr?	MM
S2				3	tr?	MM
S3	tr		tr	5		MM
S4	tr		tr	8	tr	MM
S5	tr		tr	5	tr	MM
S6 (top)	tr			5		MM

<sup>a</sup>tr = trace, MM = predominant, ? = tentative identification.

Table 2. Chemical Analysis of Column Material

Sample Number	Fe (percent)	Mn (mg/kg)	U (mg/kg)	Residual <sup>c</sup> (mg/kg) (percent)	Total (percent)
<b>Microwave Digestion With HNO<sub>3</sub></b>					
S0 (original)	80.6	4,680	7.1 <sup>a</sup>	9.43	90.50
S1 (bottom)	80.7	4,400	791 <sup>a</sup>	9.44	90.58
S2	74.5	4,850	3,730 <sup>a</sup>	8.18	83.17
S3	80.4	4,750	3,310 <sup>a</sup>	8.32	89.53
S4	81.2	5,630	3,240 <sup>a</sup>	8.22	90.31
S5	81.8	5,220	2,530 <sup>a</sup>	7.98	90.56
S6 (top)	82.8	5,310	1,680 <sup>a</sup>	8.40	91.90
<b>Concentrated HNO<sub>3</sub>, HF, and HClO<sub>4</sub> Digestion</b>					
S0 (original)	85.0 <sup>b</sup>	5,980	8.6	2.34	87.94
S1 (bottom)	84.2 <sup>b</sup>	4,590	778	1.22	85.96
S2	84.8 <sup>b</sup>	5,620	3,400	1.44	87.14
S3	84.3 <sup>b</sup>	4,940	3,050	2.62	87.72
S4	85.9 <sup>b</sup>	5,340	2,280	3.16	89.82
S5	84.2 <sup>b</sup>	5,620	2,940	2.36	87.42
S6 (top)	85.3 <sup>b</sup>	4,940	1,420	3.54	89.48

<sup>a</sup>Spiked sample recovery and duplicates are not within limits.

<sup>b</sup>ICP serial dilution is not within limits.

<sup>c</sup>Weight of the undigested portion of the sample.

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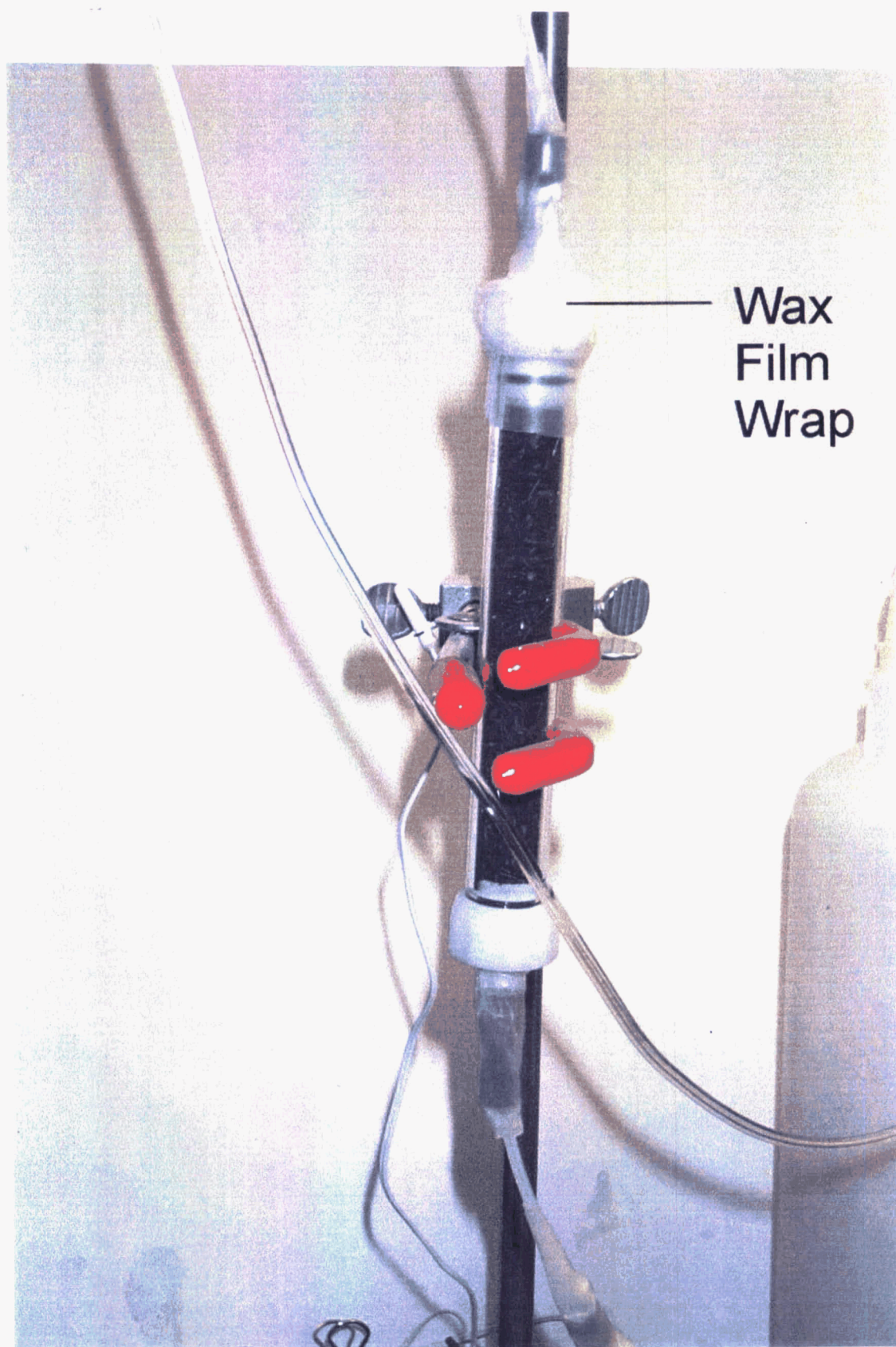


Figure 1. Column Containing ZVI



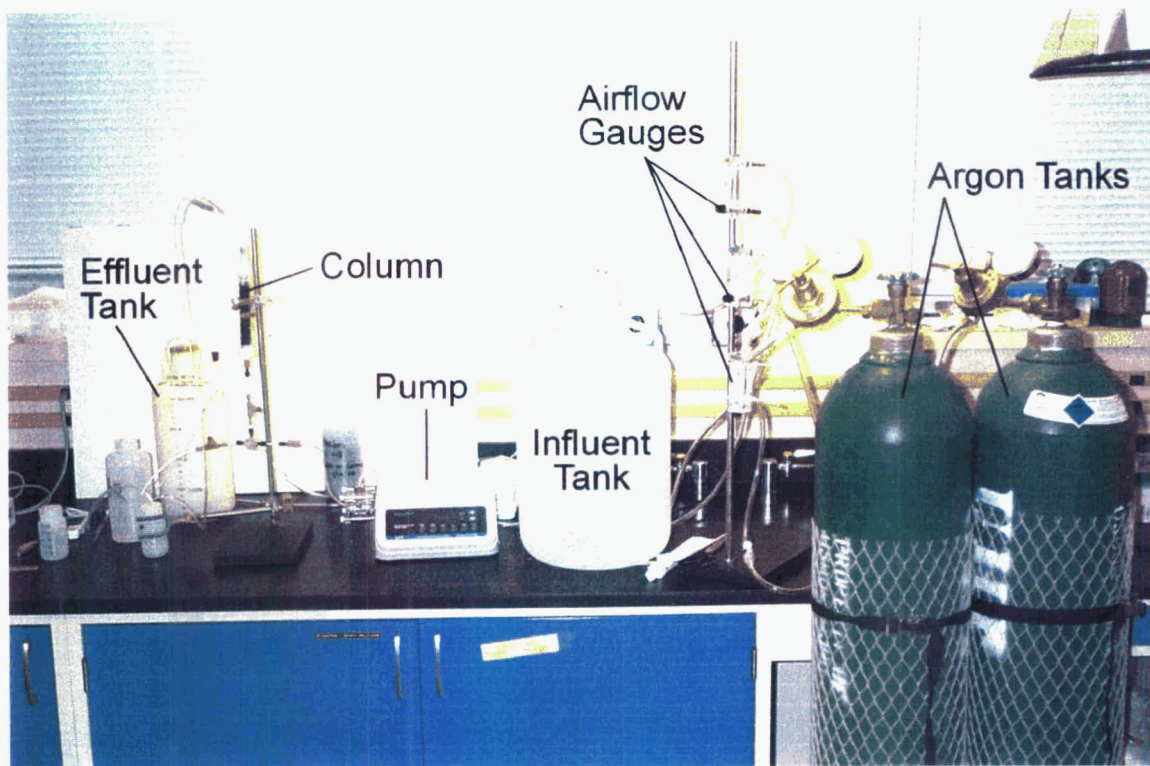


Figure 2. Experimental System



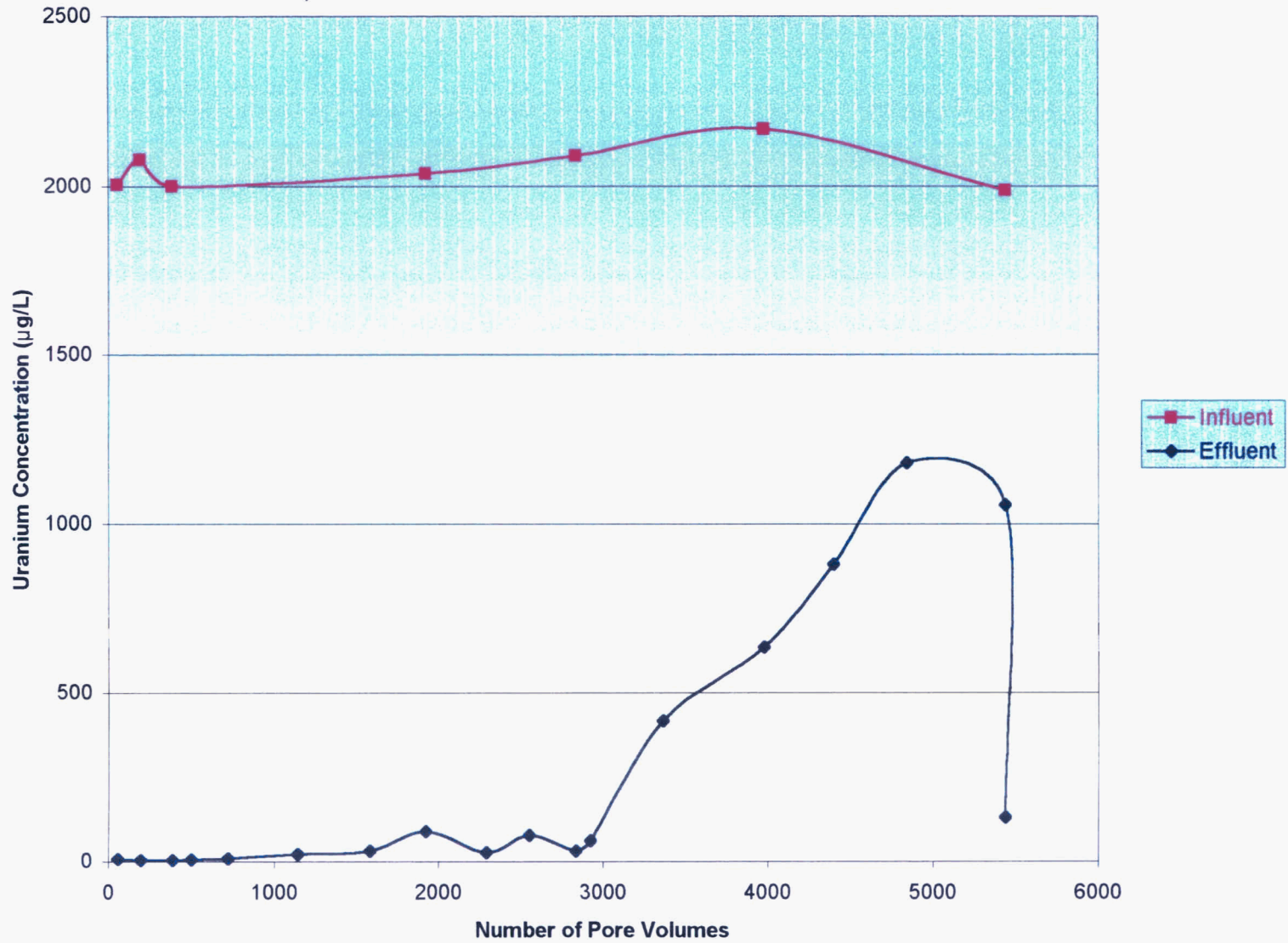


Figure 3. Uranium Concentrations in Column Influent and Effluent

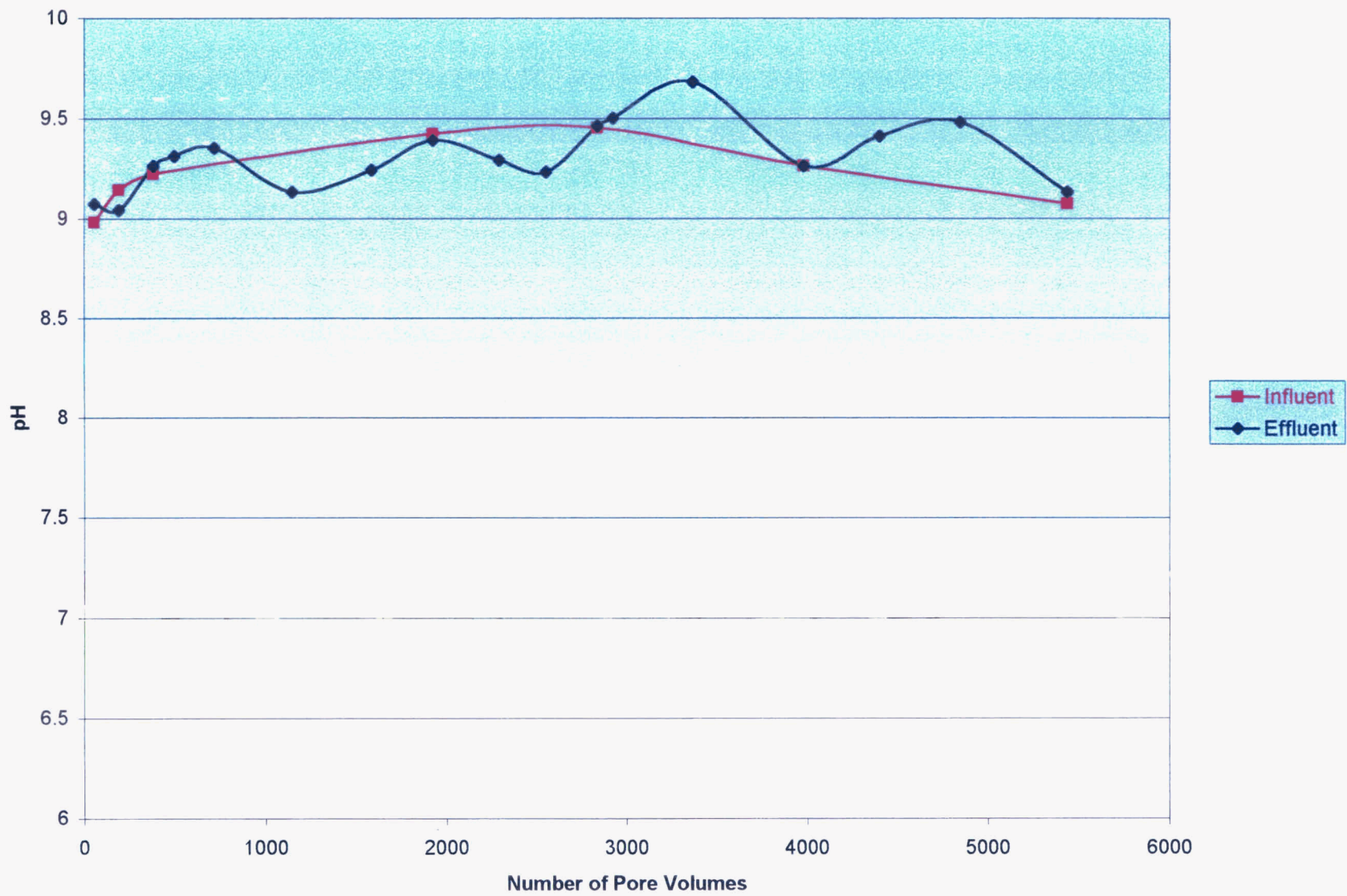


Figure 4. pH Values of Column Influent and Effluent

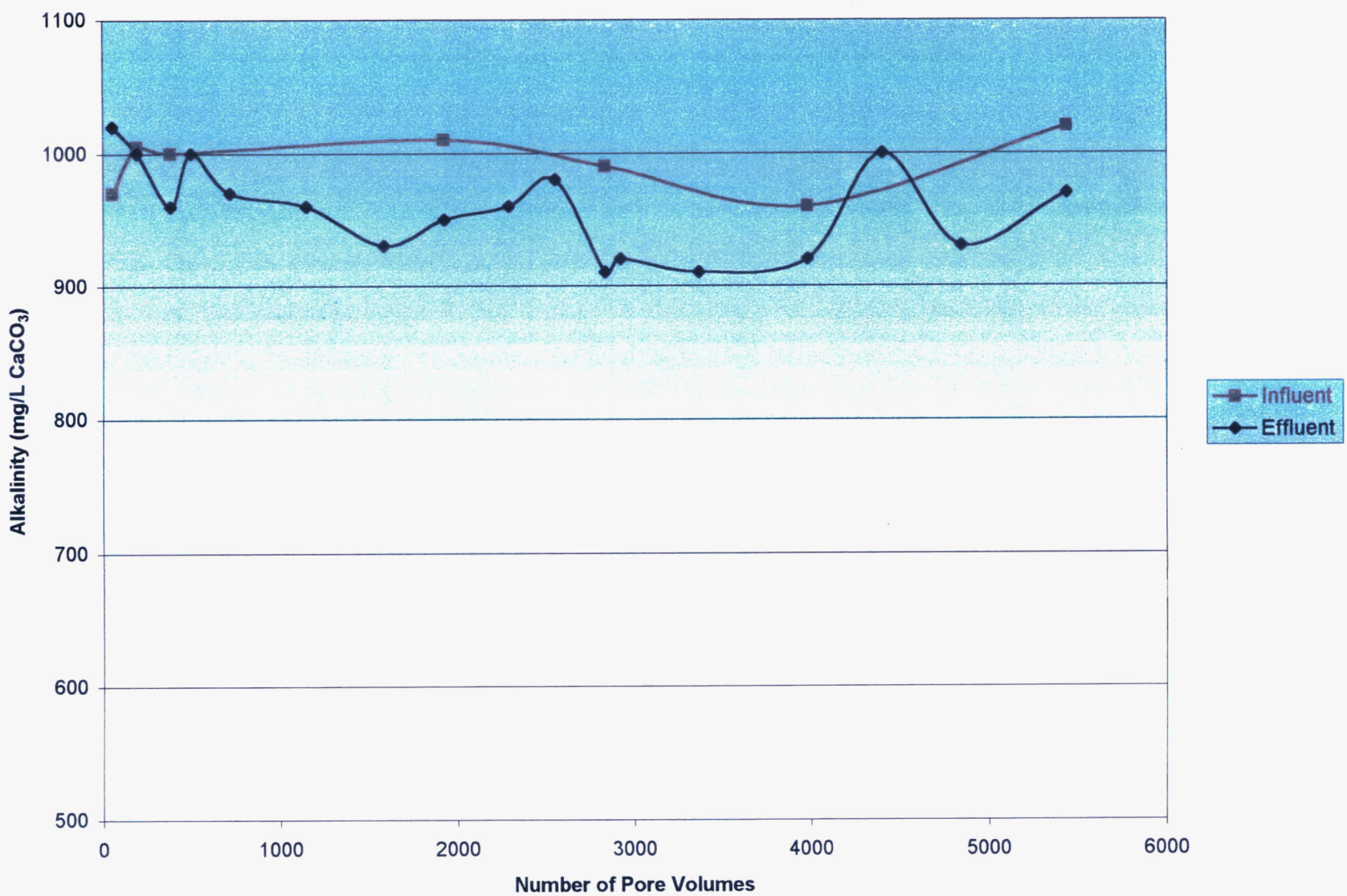


Figure 5. Alkalinity in Column Influent and Effluent



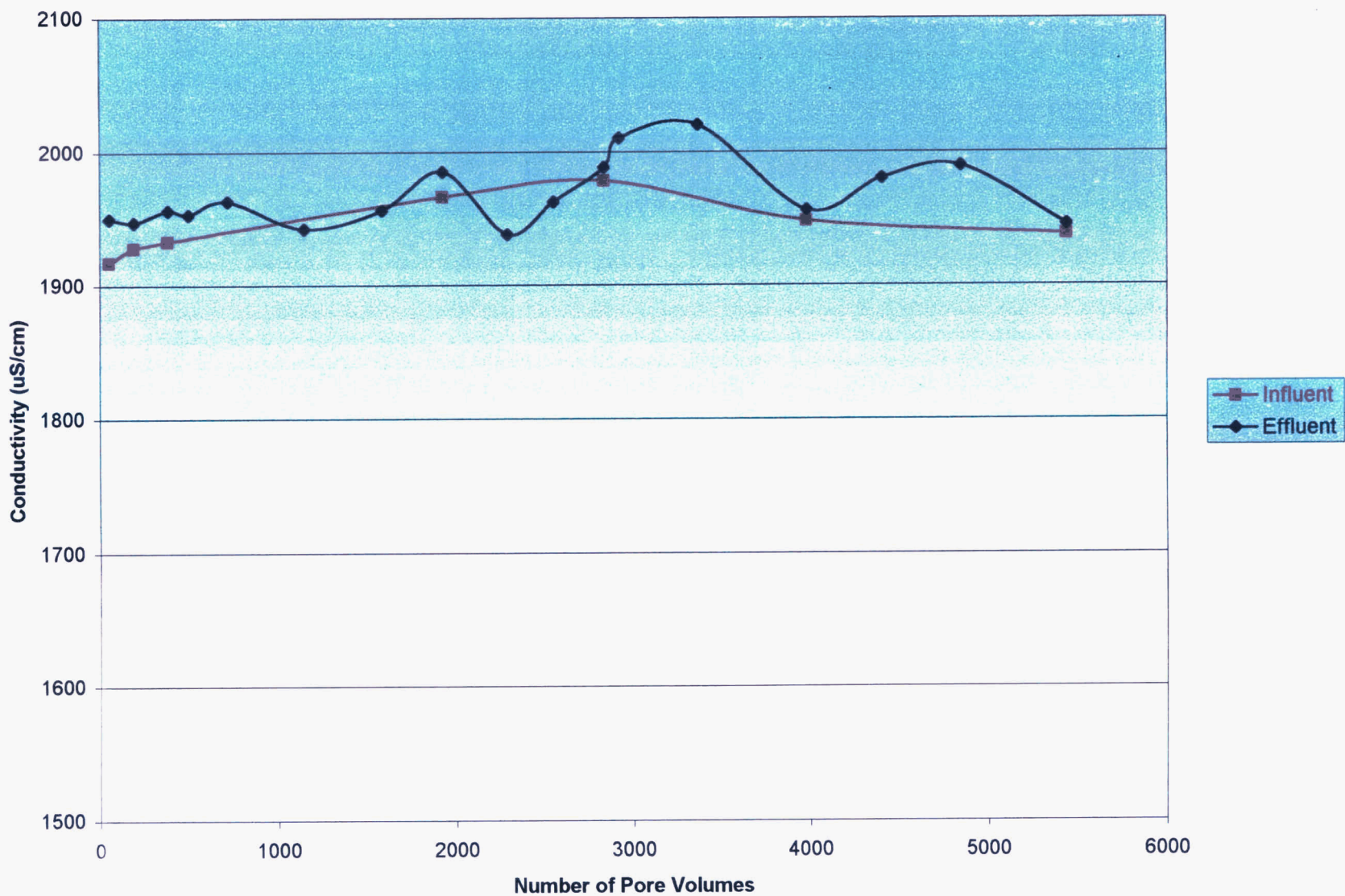


Figure 6. Conductivity in Column Influent and Effluent



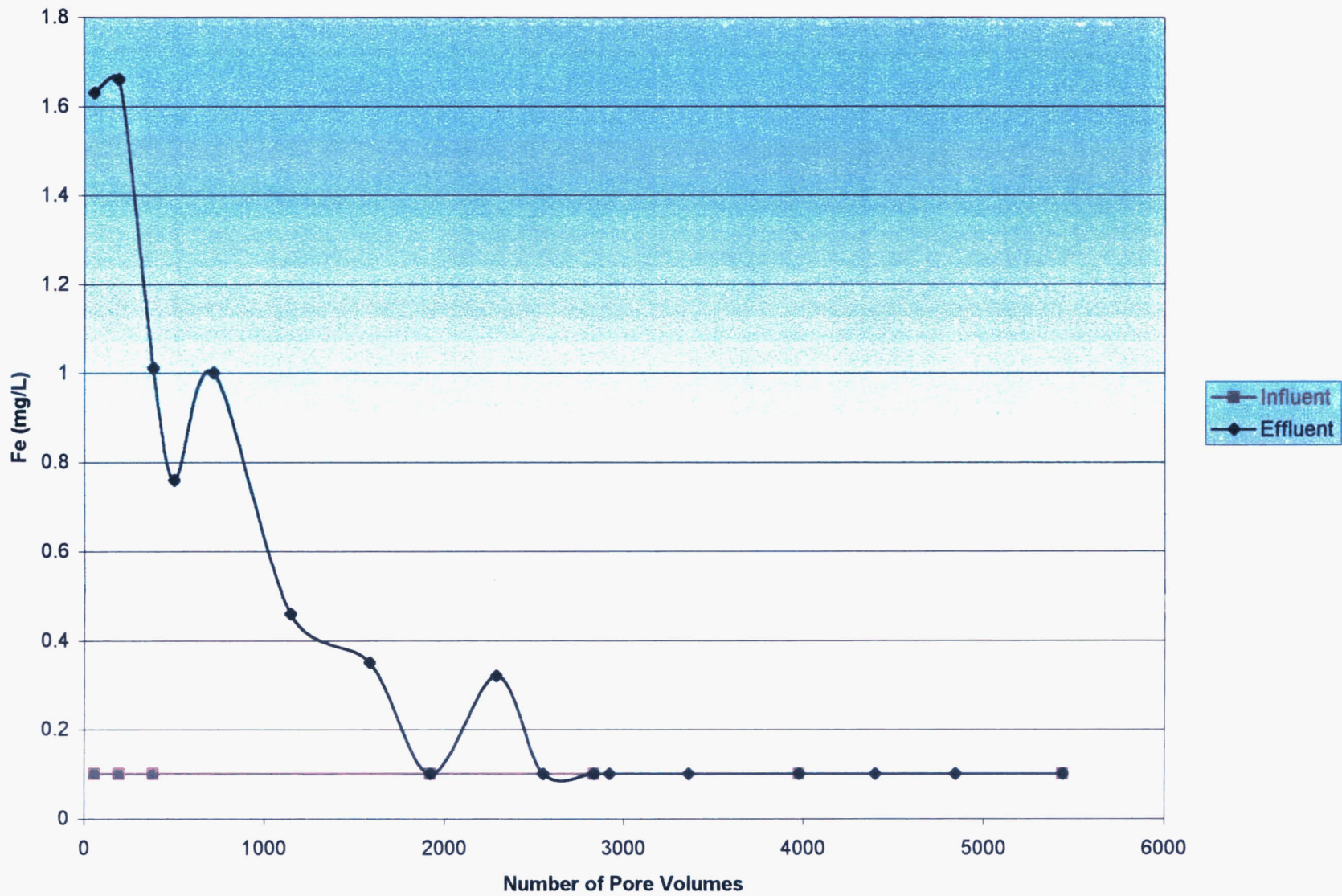


Figure 7. Iron Concentrations in Column Influent and Effluent

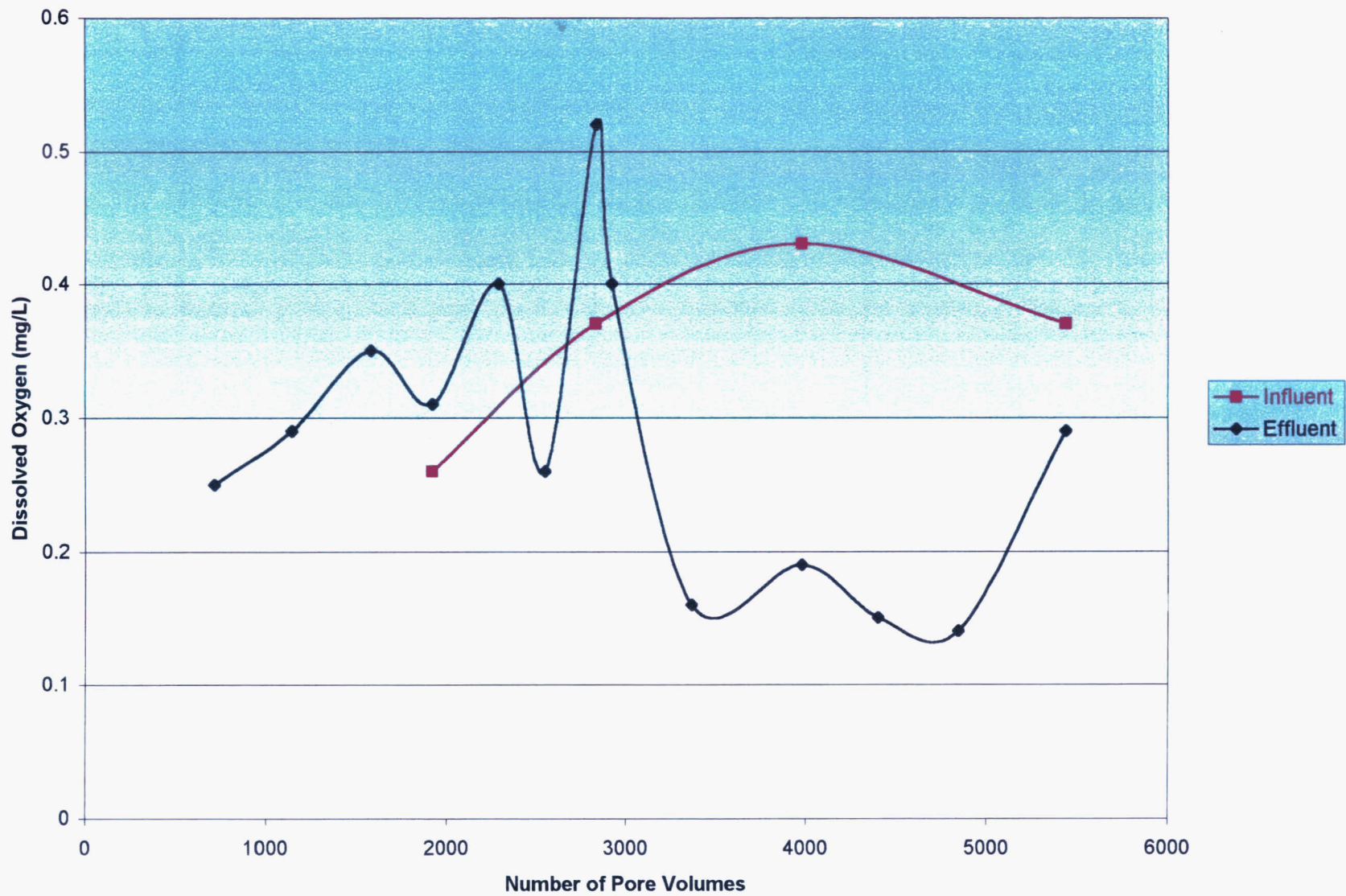


Figure 8. Dissolved Oxygen Concentrations in Column Influent and Effluent



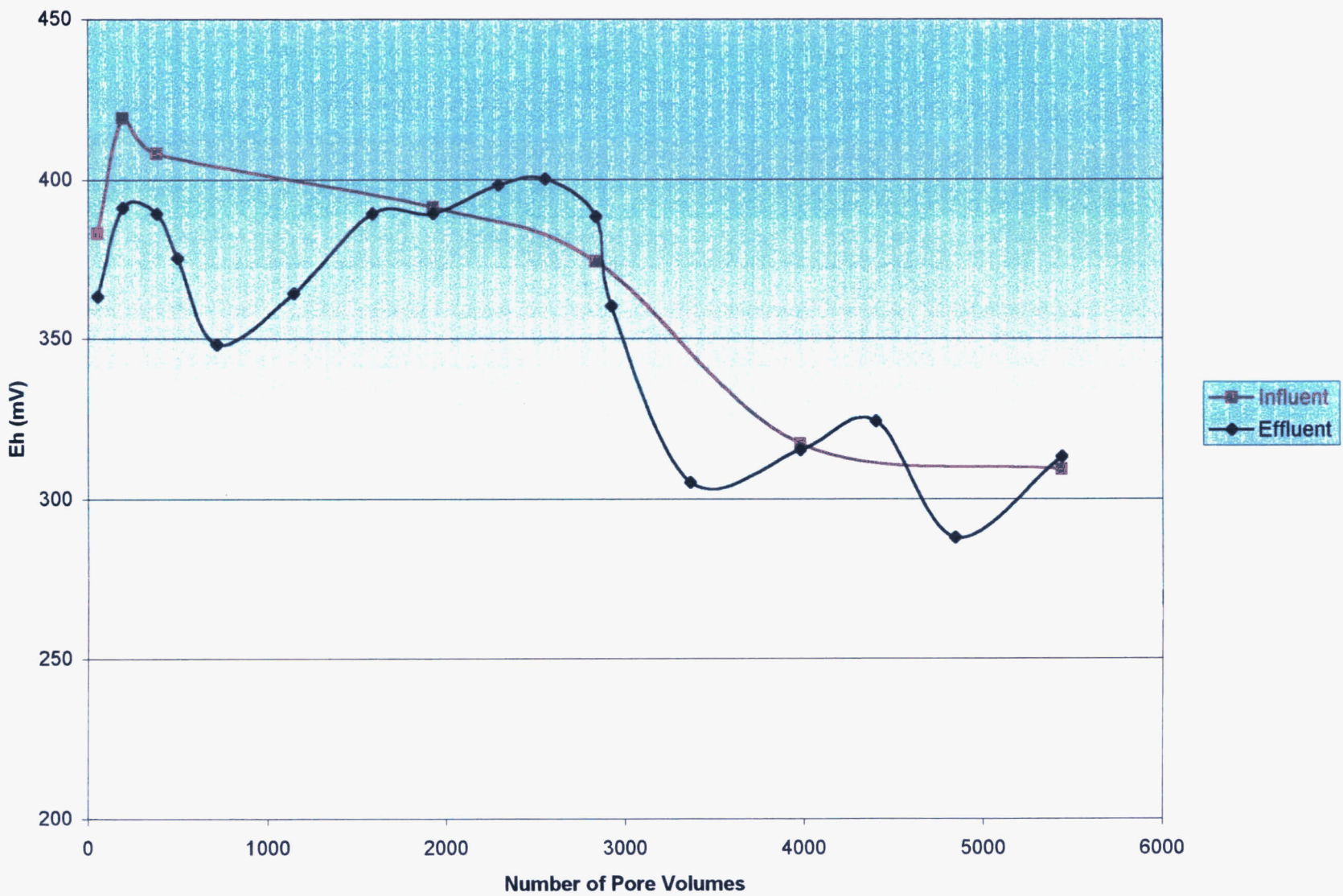


Figure 9. Eh Values of Column Influent and Effluent





**Appendix A**

**Environmental Sciences Laboratory Work Submittal**

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WORK SUBMITTAL TO ENVIRONMENTAL SCIENCES LABORATORY

Submittal Date January 10, 2000 Date Required March 30, 2000  
Submitted By Staw Morrison Signature Staw Morrison  
Formal Report Required (check one)? Yes X No       
Project: PERT Wall Mont. - Manuscript Charge No. 342003003 PERT Wall  
Analysis Type (check one): Kd      Leaching      Other X manuscript

Sample Numbers Experiments will use ZVI

Analytes U and others AS Requested

Solution Composition TBD, Probably a Synthetic water with  
high bicarbonate

Comments (attach procedure if needed)  
See attached procedure

Tracking (ESL use only):

Actual Labor Hours (ESL use only):

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## EXPERIMENTAL PLAN

### Mechanisms of Uranium Removal by ZVI

January 12, 2000

#### Background

An experiment is planned in support of a manuscript being prepared for the Monticello PRB project. The purpose of the experiment is to better understand the chemical mechanisms responsible for uranium uptake by ZVI.

Two hypotheses have been suggested to explain the primary chemical mechanism for uranium uptake by ZVI: (1) reductive precipitation, and (2) adsorption. Reductive precipitation refers to the formation of low-solubility uranium minerals in response to low redox conditions. In the second hypothesis, ZVI oxidizes to ferric oxyhydroxide minerals and uranium is adsorbed on the oxyhydroxides.

ZVI oxidizes readily to ferric oxyhydroxide in the presence of oxygen. In an oxygen-free environment, however, ferric oxyhydroxide should not form. Therefore, if hypothesis 2 is correct, ZVI should not remove uranium from an anaerobic solution. Uranium does not adsorb to ferric oxyhydroxide from solutions with high carbonate concentrations and high pH.

#### Purpose

The purpose of the experiment is to determine if ZVI is effective at removing uranium in an anaerobic, high carbonate, high pH environment. High uranium removal under these conditions supports the first hypothesis.

#### Procedure

- (1) *Prepare Synthetic Water (SW)*. Add 234 mg C (1638 mg/L of  $\text{NaHCO}_3$ ) per liter of deionized water (these are the concentrations used in a set of experiments in Morrison et al, 1995 and insures that ferric oxyhydroxide will not adsorb uranium). Add 2 mg/L uranium (200  $\mu\text{L}$  of 10,000 mg/L U in 1 liter) as uranyl nitrate. Add 100 mg/L of sodium azide ( $\text{NaN}_3$ ) to curtail microbial activity. Adjust pH, to 8.8 (keep pH within 0.2 units throughout the experiment) with sodium hydroxide. Check to be sure pH remains in this range for at least 12 hours and that all  $\text{NaHCO}_3$  is dissolved. Measure alkalinity.
- (2) *Prepare Anaerobic Apparatus*. Use a 20 L carboy to hold the influent SW. Use a cap fitted with a hose barb and an opening for a gas line. Connect the hose barb to a plastic pipe that extends to the bottom of the carboy (this is the influent line). Connect the gas line to a high-purity argon tank. Connect a flow gauge to measure argon flow into the source tank. Connect the argon line from the argon tank to an



aquarium stone placed on the bottom of the effluent tank. Place a capped 4-liter collection bottle at the effluent end of the column. Drill 2 holes in the cap to the effluent bottle just large enough for the effluent hose and an argon line. There is a rigid 4-L Nalge container with 3 custom holes (one can be plugged with a black stopper) that is perfect for this. Connect a flow gauge to measure argon flow to the effluent tank. Use a Y connection off the argon tank to connect to the effluent line. Plumb a 22 mL OMNI glass column. Use Tygon tubing to connect the hose barb on the source tank to a peristaltic pump and then to the bottom of the column; place a valve (inlet valve) about 2 inches from the inlet to the column. Use a temperature meter to determine minimum and maximum temperatures daily. Use parafilm on all joints with liquid flow to help prevent oxygen influx. Flush system out with 20%  $\text{HNO}_3$  followed by DI. Flush out residual liquid with argon to dryness. Take a photo of the completed system.

- (3) *Fill Columns.* Weigh the dry column. Place ZVI (-8 +20, same as was used at Monticello) in the OMNI column. Tamp lightly and fill completely. Determine weight of ZVI by difference. Take a photo of the ZVI.
- (4) *Conduct experiment.* Measure parameters (pH, ORP, DO, conductivity, alkalinity, uranium) on the SW (collect sample at the inlet valve) then purge source tank with argon (150 mL/min) for at least 24 hours. Purge column with argon (40 mL/min) for at least 24 hours. Measure parameters again. Flush argon through the source tank at 150 mL/min and through the effluent at 40 mL/min throughout the experiment to maintain the solution oxygen free. Using the peristaltic pump, pass SW through the columns at 2 mL/min (residence time of about 5 minutes) into the column. Determine the volume required to fill column (this is the pore volume).
- (5) *Sample Collection.* Collect samples at 6, 12, 18, 24, 36, and 48 hours and then every 24 hours for at least 5 days (or until breakthrough if possible, which may take weeks). Collect a 100 mL sample to make the measurements (use a capped Nalge bottle with 2 hole and uprge with argon). Measure pH, ORP, DO, conductivity, alkalinity, iron, and uranium concentration in the effluents. Take care to limit exposure to the air during sample collection and measurement. Keep the sampling container under argon as much as possible. Flush argon across the top while sampling. After opening, first sample 25 mL for U and Fe analysis (preserve with 2%  $\text{HNO}_3$ ). The sample should not be touched by probes of any kind prior to U sampling. Next, insert the ORP probe (still with argon). Then DO, alkalinity (pH), and conductivity in that order. Record the minimum and maximum temperatures daily.
- (6) *Solids Analysis.* After the experiment is completed, examine the solid ZVI microscopically for indication of red-coloration (ferric oxyhydroxide). Take photos. Place in a 50-,L tube, seal under argon with parafilm and double bag with argon. Send to lab for XRD analysis. Include a sample of the fresh ZVI also.



**Appendix B**

**Environmental Sciences Laboratory Notes**



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MPeT01-02-01

[illegible]

5. Morvin



MPWI

MPET01-02-02

2

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1416	Another 4L batch	pH = 8.78		(280 mL 10N NaOH)								
2	1524	Continued making 4L batches.	all had pH = 8.78										
3													
4	HARDED PEER-001	→ ZVI Peerless -8 +18	Kept a 1 L Nalge bottle of it (with date = 1/12/00)										
5		Column weight = 78.4g											
6		Column + ZVI = 115.4g											
7		Weight of ZVI = 37.0g											
8													
9		Gently tamped while filling											
10													
11	1600	Started Argon flow to source tank (250 mL/min) and to column (250 mL/min)											
12													
13		measured SW in Carboy											
14		ALK = 950 mg/L CaCO <sub>3</sub>											
15		U <sub>e</sub> = 2.07 mg/L											
16		pH = 8.82											
17													
18													
19	1/13/00	950	Argon still flowing to source tank and column (~17 hours)										
20		Filled lines with SW → capacity from source tank to											
21		column bottom is less than 3 mL.											
22													
23		T = 60.8°F, MAX = 68.5°F 59.5° = min											
24													
25													
26	1130	Started flow into column of ZVI (2 mL/min)											
27		Time to fill column = 6.7 mins											
28		1 PORE VOLUME = 13.4 mL call it 13											
29													
30	1647	Begin MPWI-001E sample collection											
31													

S. Morrison

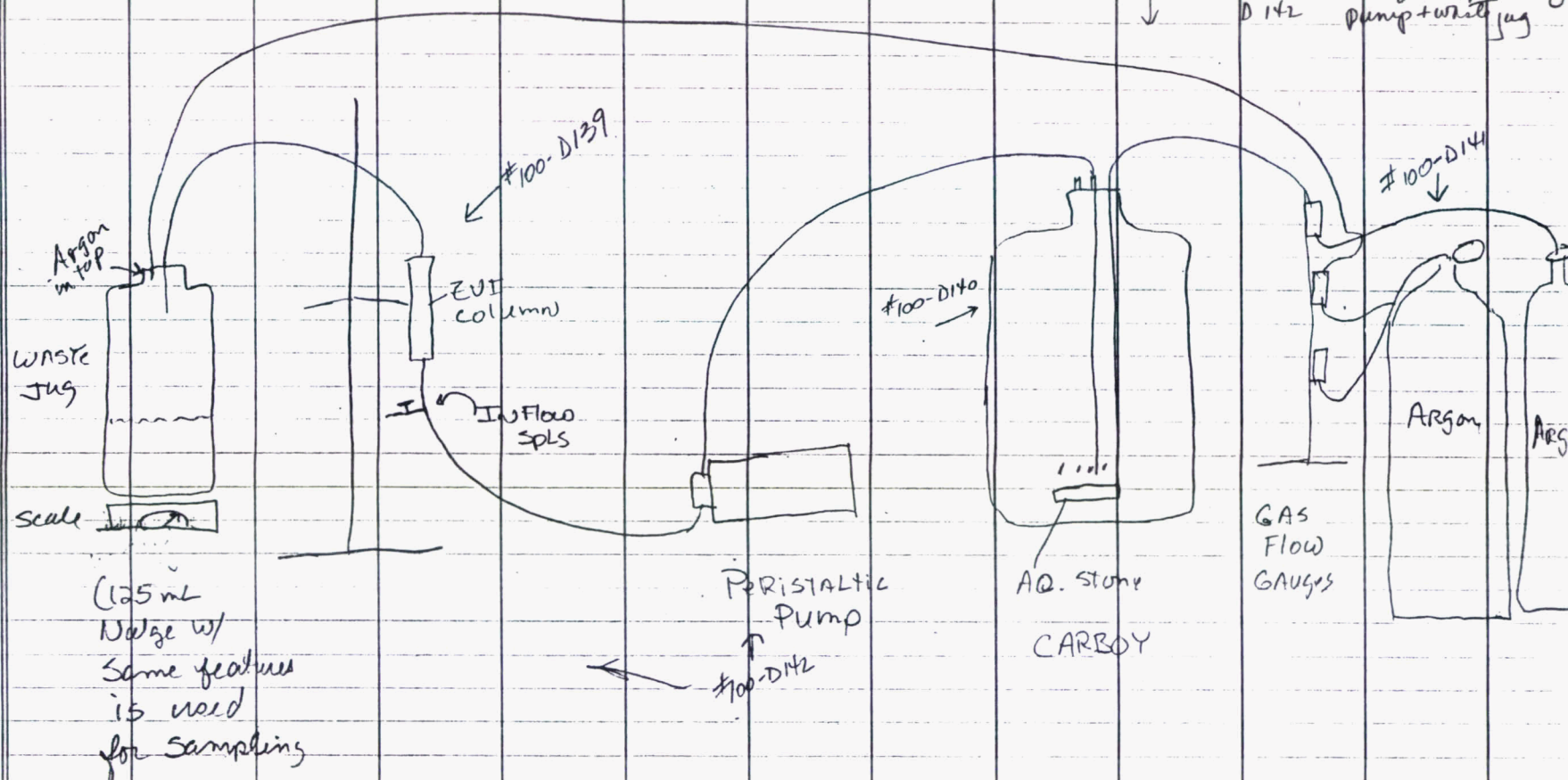


MPW1

MPeRT 01-02-03

Sketch of Final Setup

PHOTOS: #100 - D138 Full system  
#100 - D139 Column  
D140 bubbling carbonyl  
D141 Argon w/ pressure ga  
D142 pump + waste jug



J. Morrison



MPWI-

MPGT01-02-04

2

	1	2	3	4	5	6	7	8	9	10	11	12	13
1/13/00 1800	Begin MPWI-0015 Sample collection. ↑ rate to 3.6 mL/min for this												
1830	End sample collection return rate to 2 mL/min												
1/14/00 0820	Check Retup. Ar flows steady Tank 1 = 1575 psi Tank 2 = 2100 psi												
	Source tank @ 21 L Temp 67.6°F Hi 75.7°F Min 60.8°F												
	Calibrate YSI 3500 X14292 pH 4.7 Zobel = +220												
0910	Begin MPWI-002E sample collection. Flush bottle & Ar prior to start												
1009	End sample collection 110 mL												
1022	Begin MPWI-0025 sample collection. Flush bottle & Ar prior to start. ↑ flow rate												
	to 3.6 mL/min.												
1052	End sample collection. Return rate to 2 mL/min. Switch valves. Effluent to waste jug												
1/15/00 0845	Arrive @ Lab. Tubing was leaking @ pump head. Prepare new pump head and												
	tubing. Stop flow to column x 2 minutes - shut valve @ column base. Replace												
	pump head/tubing. Flush line with source water. Reconnect to column open												
	Valve. No leaks. Ar flow steady Tank 1 = 1575 psi Tank 2 = 2050 psi												
	Source tank @ 18 L Temp 68.0°F Hi 73.9°F Lo 67.1°F												
0900	Begin MPWI-003E sample collection. Flush bottle & Ar prior to start.												
	empty waste jug. Note: ± 50 mL lost to tubing failure.												
	Cal YSI 3500 X14292 pH 4.7 Cal Orion 520A S11042 Zobel = +228												
0950	End sample collection 100 mL												
1000	Begin MPWI-0035 collection flush & Ar prior to start. ↑ rate to 3.6 mL/min												
1030	End sample collection. Return rate to 2 mL/min. Switch valves. Effluent to waste jug												
1/16/00 0958	Start sample collection MPWI-004E. Flush w/ Argon 5 min (room temp) Calibrated												
	pH 4, 7, 10. Zobel = 228 mV. Effluent tubing is red despite changing it 2 days												
	ago (some Fe is moving and being oxidized in the tubing. Effluent is												
	clear however. Did not measure DO. Waiting on an acceptable probe.												
	Ar to source tank = 400 mL/min. Ar to outflow = 450 mL/min (left them as is).												
	Emptied waste tank. No obvious red color in ZVI. Room temp = 69.6°C; min = 67.3, max = 71.3												

J. Morrison





MPRT01-02-05

②

MPWI-

	1	2	3	4	5	6	7	8	9	10	11	12	13
1/17/00 0930	2	3	4	5	6	7	8	9	10	11	12	13	
	Start MPWI-005E. flush bottle = Ar prior to start												
	Source tank 12L Ar tank 1 = 1825psi Ar tank 2 = 1825psi												
	temp 70.5°F max = 70.5 min 68.5												
	waste = 2764 g net												
	cal YSI pH 4, 7, 10 zobel +225												
1/17/00 1830	DO measurements. YSI Model 55 Probe												
	Instrument check												
1/18/00 0745	System working well. 9.5L in source jug. Ar Tank 1 = 1700psi Tank 2 = 1700psi												
1015	Start Ar flow to new source tank <sup>(#2)</sup> = fresh 22L of 3W. Will bubble overnight before switching out @ 0.6 Lpm												
1030	Empty waste jug. Switch to larger waste collection jug. Ar flow rate to 1 Lpm												
	temp 71.8° max 72.3 min 69.4 reset thermometer												
	No samples today												
1/19/00 0745	Arrive @ Lab. system working well. Ar tank 1: 1600psi Tank 2 = 1300psi												
	temp 68.4° max 72.0 min 68.2. Switch to new source tank.												
	flush sample bottle = Ar. Slight discoloration @ base of column. minimal change.												
0730	Begin MPWI-006E sample collection												
	empty waste jug cal YSI 3500 4, 7, 10 zobel +233												
0820	End sample collection. Switch outflow to waste jug												
1/20/00 1000	System working well. 20L in source tank Ar tank 1 = 1450psi Tank 2 = 900psi												
	temp 70.2°F max 73.8°F min 67.5°F												

J. Morrison



MPerT01-02-06

	1	2	3	4	5	6	7	8	9	10	11	12	13
1/4/00 0700	system working well.	Ar tank 1 = 1350psi	Tank 2 = 600psi	Source tank	17.5L								
2	temp 68.9°F	max 72.7°F	min 68.5°F										
0705	Begin MPW1-007E sample collection.	flush bottle = Ar prior to start											
4	cal YSI 3500 pH 4, 7, 10	spheel = +232											
5	empty waste jug												
6													
1530	Change Ar Tank #2	2350psi											
8													
1/24/00 0730	system working well	Ar tank 1 = 1000psi	Tank 2 = 2150psi										
10	temp 68.4°F	max 72.5°F	min 66.4°F										
11													
0755	Begin MPW1008E sample collection.	flush bottle = Ar prior to start											
13	cal YSI 3500 pH 4, 7, 10	spheel = +232											
14	Empty waste jug	8554ml											
0845	End MPW1008E sample collection	Effluent to waste											
16													
0900	Begin MPW1-0045 sample collection.	flush bottle = Ar prior to start.											
18													
0930	End MPW1-0045 sample collection.	Return rate to 2.0 ml/min.	switch valves.										
20													
0945	Prepare 22L of SW.	Begin Ar bubble @ 0.6 lpm.	Tank #3										
22													
1/25/00 1615	Column has run well all day.	Switch to new source tank #3.											
24	Ar tank 1 = 1650psi	Tank 2 = 1850psi											
25	temp 70.7°F	max 72.1°F	min 68.4°F										
26													
1/26/00 1100	Column running well.	Ar tank 1 = 800psi	Tank 2 = 1400psi	Source tank = 21+L									
28	temp 68.4°F	max 72.1°F	min 68.4°F										
29	Begin MPW1-009E sample collection	flush bottle = Ar prior to start											
30	empty waste jug	8454ml											
1200	End sample collection	Effluent to waste											

S. Morrison





MPERT 01-02-07

	1	2	3	4	5	6	7	8	9	10	11	12	13
1/26/00 1200	2	Cal YSI 3500	pH 4, 7, 10	zohel = +231	Measure parameters on MPWI-009E								
1/27/00 1400	4	System working well. Change Ar tanks											
1/28/00 0900	6	System working well. Begin MPWI-010E sample collection. Flush bottle = Ar prior to start											
	7	18 L in source tank Ar tank 1 = 2400psi Tank 2 = 900psi											
	8	temp 67.1°F max 72.3°F min 66.0°F											
	9	empty waste jug. Flow rate has ↓ to 1.22 ml/min. Will ↑ rate on pump p sample collection											
	10	cal YSI 3500 pH 4, 7, 10 zohel = +234											
1020	12	End MPWI-010E sample collection ↑ pump rate to 2.25 ml/min											
12/30 1010	14	Column running well Ar tank 1 = 2200psi Tank 2 = 500psi. Will change #2 out tomorrow											
1/31 0730	16	Column running well Ar tank 1 = 2050psi Tank 2 = 400psi. Will change											
	17	14+L left in source tank											
	18	temp 66.6°F max 72.7°F min 65.3°F											
0745	20	Begin MPWI-011E sample collection. Flush bottle = Ar prior to start.											
	21	cal YSI 3500 pH 4, 7, 10 zohel = +233											
1030	23	End MPWI-011E sample collection. Eff. to waste											
1045	25	Begin MPWI-005S sample collection. Flush bottle = Ar prior to start. A flow rate to 3.6 ml/min											
1200	27	End MPWI-005S sample collection & leave pump @ 3.6 ml/min. Call flow rate 1.33											
2/1 0750	29	Stop pump. Tubing plugged.											
2/2 0905	31	Replace tubing resume flow. Measure outflow from 1/31 @ 1200 to 2/1 @ 0750											
		0.42 ml/min											
		1290 minutes / 510 ml											
		12/12											

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MPRT 01-02-08

	1	2	3	4	5	6	7	8	9	10	11	12	13
2/2/00 1345	Begin MPWI-012E sample collection. Flush bottle & Ar prior to start.												
	2	Cal Orion S20A for ORP zobel = +231.5				Cal Orion S20A for pH 4.7							
	3	13L in source tank. temp 72.7°F max 73.8°F min 66.0°F											
	4	Ar tank 1 = 1800psi Tank 2 = 2100psi											
1435	End MPWI-012E sample collection. Effluent to waste.												
2/3/00 0730	Column running well Ar tank 1 = 1700psi Tank 2 = 1950psi												
	8	temp 68.7°F max 73.4 min 66.0				11L in source tank							
2/4/00 1045	Column running well Ar tank 1 = 1550psi Tank 2 = 1700psi												
	11	7.5L in source tank											
	12	temp 70.5°F max 73.9°F min 66.6°F											
	13	Begin MPWI-013E sample collection. Flush bottle & Ar prior to start.											
	14	Empty waste jug											
	15	Cal Orion S20A's pH 4.7, 10 ORP = +233											
	16	DO zero cal soln = 0.02 mg/L											
1135	End MPWI-013E sample collection. Effluent to waste												
	18	prepare 20+L SW. Begin Ar purg @ 0.5 Lpm											
2/6/00 1035	Column running well. ± 1L left in source tank. Switch to new source tank 22+L												
	21	temp 69.1°F max 72.7°F min 66.2°F				Ar tank 1 = 1300psi Tank 2 = 850psi							
	22	will not change tank till AM. Hopefully Ar will be delivered and won't have to switch to N <sub>2</sub>											
2/7/00 0750	Column running well 20+L left in source tank												
	25	temp 66.6°F max 73.9°F min 66.4°F				Ar tank 1 = 1200psi Tank 2 = 650psi							
0800	Begin MPWI-014E sample collection flush & Ar prior to start.												
	28	Empty waste jug											
	29	Cal Orion S20A pH 4.7, 10 zobel = +235.6				DO zero cal 0.09							
0850	End MPWI-014E sample collection. Effluent to waste												

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MPERT01-02-09

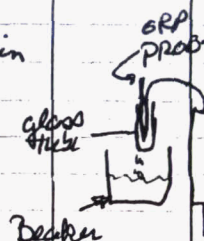
	1	2	3	4	5	6	7	8	9	10	11	12	13
2/7/00 0900	2	3	4	5	6	7	8	9	10	11	12	13	
Begin MPWI-006S sample collection. Flush bottle = Ar prior to start. ↑ pump rate to 3.6 ml/min.													
0930	5	6	7	8	9	10	11	12	13				
End MPWI-006S sample collection. Effluent to waste jug. ↓ pump rate to 2.0 ml/min													
2/8/00 0810	7	8	9	10	11	12	13						
Column running well Ar tank 1 = 1100psi tank 2 = 350psi have called again re Ar delivery temp = 66.4°F max 73.9°F min 66.4°F													
2/9/00 0725	10	11	12	13	14	15	16	17	18	19	20	21	22
Column running well. Ar tank 1 = 950psi Tank 2 = 150psi. Will change to N <sub>2</sub> - No Ar available tr 2/14 temp 68.4°F max 73.0°F min 67.5°F 15L in source tank													
0730	13	14	15	16	17	18	19	20	21	22	23	24	25
Begin MPWI-015E sample collection. Flush bottle = Ar prior to start. Cal Orion 520A pH 4.7, 1.0 20ml = +235.5 DO zero = 0.07 mg/L													
0820	16	17	18	19	20	21	22	23	24	25	26	27	28
End MPWI-015E sample collection. Effluent to waste													
0910	18	19	20	21	22	23	24	25	26	27	28	29	30
Change tank 2 to N <sub>2</sub> 2250psi													
2/10/00 0800	20	21	22	23	24	25	26	27	28	29	30	31	
Column running well													
2/11/00 0945	22	23	24	25	26	27	28	29	30	31			
Column running well Ar tank 1 = 700psi N <sub>2</sub> tank 2 = 1750psi 9.5L in source tank temp 71.2°F max 73.8°F min 65.5°F													
1006	25	26	27	28	29	30	31						
Begin MPWI-016E sample collection. Flush = Ar prior to start Empty waste jug													
1055	27	28	29	30	31								
Cal Orion 520A 20ml = +234.7 pH 4.7, 1.0 DO zero 0.07 mg/L End MPWI-016E sample collection Effluent to waste jug													
2/13/00 0940	31												
Change to new sm Start N <sub>2</sub> flow to new source jug for purge													

S. Morrison

J. Morrison

MPERT 01-02-10

	1	2	3	4	5	6	7	8	9	10	11	12	13
2/14/00 0940	Switch to new source tank												
0805	Begin MPWI-017E sample collection. Purge = N <sub>2</sub> prior to collection. 224L in source tank Ar tank 1 = 350psi N <sub>2</sub> tank 2 = 650psi temp 68.5°F max 72.9°F min 67.5°F												
	Cal Orion SLOA pH 4.7, 10 Zobel = +035.6 Dosage check = 0.11 mg/L												
0905	End MPWI-017E sample collection. Effluent to waste												
	END OF EXPERIMENT - Kept pumping fluid @ 2 mL/min												
1430	Rigged up a (~25 mL) glass tube for "flow-through" cell Overflows into a beaker. ORP is measured with the new 9178 probe (Zobel = 190 mV) w/ 900001 full 50W.												
	Problem - Are we getting accurate ORP measurements? Air space is purged w/ N <sub>2</sub> . Purged at 3.6 mL/min until probe wet.												
1438	ORP = 136.7 mV												
1442	ORP = 137.0												
1520	ORP = 102.8 mV (starting to overflow)												
1627	ORP = 95.9 mV Adjusted flow to 0.2 mL/min												
1654	ORP = 102.8 mV												
3/15 0735	ORP = 44.1 mV												
0753	ORP = 44.4 mV. Shut pump off. collected sample MPWI-018E for U analysis												
0810	Started flushing N <sub>2</sub> through column to drain and dry. Flushed from top.												
4/7 0530	N <sub>2</sub> still flushing Tank has 1900psi												
5/1 1509	Removed column. Prepared for XRD and thin sectioning												



S. Morrison



MPERT01-02-11

2/16/00

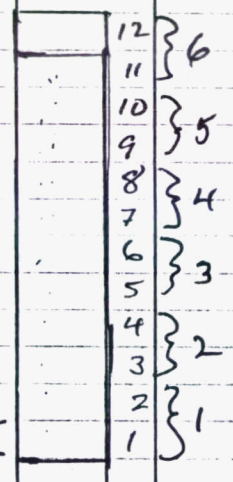
Visual (microscopic) examination of Solids

MACROSCOPIC: Reddish zone (smear on tube) <sup>amorphous smeared</sup> is confined to bottom 1cm. Actually under hand lens, the color is more greenish (under microscope there is some red). Ferric or ferrous hydroxide.

The <sup>rest of the</sup> remaining ZVI is gray. Small patches of green amorphous material near top of column.

Samples: <sup>solids</sup>  
 MPW-S-1 Bottom 2cm  
 MPW-S-2 next "  
 MPW-S-3 "  
 MPW-S-4 "  
 MPW-S-6 Top 2cm  
 MPW-S-0 Fresh (unused) ZVI

Green/red zone =



Descriptions (Binoc microscope): All samples have distinct grains (laths and curls). The unused sample (MPW-S-0) has shinier surfaces with some coatings of deep red color (hematite?). The first bottom sample (MPW-S-1) has significant dustings of yellow (limonite?) and the surfaces are duller in appearance. Sample MPW-S-4 has very dull appearing surfaces (looks like it could be significantly altered), they have dull gray almost ash-like appearance; occasional shimmering blue color (like bornite).

Samples sent for XRD and polished thin sections.

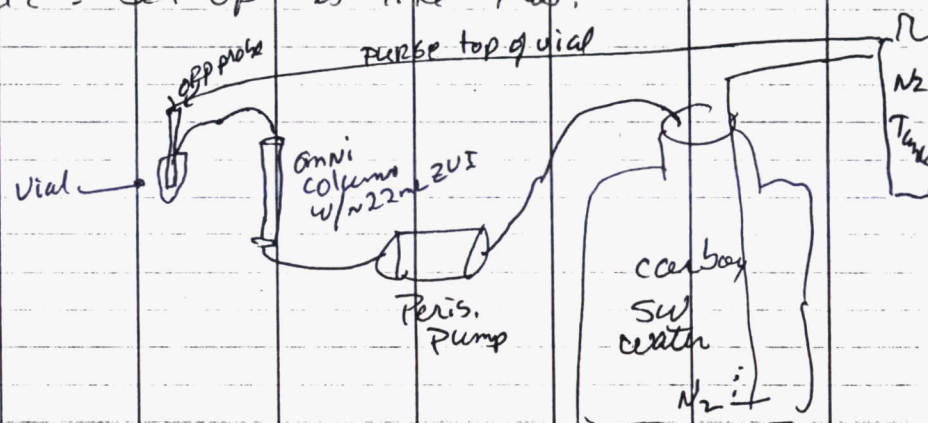
S. Morrison

MPERT01-02-12

2/17/00

0900 Purged large carboy of SW<sup>n</sup> w/ N<sub>2</sub>. Set up new column Omni small filled with Peerless-8 + BB ZVI (PEER-00-01). Did not weigh. I only want to examine Redox state. Set up is like this:

USED ORION 9778BN ORP PROBE with 900001 fill soln.



Readings (mv)			
Time	ORP	ORP Zobell	Flow RATE (ml/min)
0934		192.8	
0937	Started pump @ 2 ml/min		
0947	FIRST flow into vial (2 ml/min)		
0951	-268		2
0954	-325		2
0959	-398		2
1006	-275		2
1007	-220		2
1008	-130		2
1009	-75		2
1010	-47		2
1011	-42		2
1012	-35		2
1014	-31		2
1018	-24		2
1027	-13		2
1035	-13		2
1043	3.9		2
1044	5.0		2

J. Morrison





EFFICIENCY LINE® 22-210

\* Reinsulated probe

MPERT01-02-13

		2ORP	3ORP	4 RATE	5	6	7	8	9	10	11	12	13
2/17	1	1046	194.5	2									
	2	1047	53*	2									
	3	1049	38	2									
	4	1050	36	2									
	5	1056	35	2									
	6	1059	35	2									
	DO Standard	ORP = 31.2 mV											
	8	1114	75*	2									
	9	1115	67	2									
	10	1325	54	2									
	11	1620	52	2									
	12	1715	44	0.2									
2/18	13	0715	27	0.2									
	14	0822	21.6	0.2									
	15	0930	23.9	0.06									
	16	1125	36.2	0.06									
	17	1158	37.9	0.06									
	18	1212	20.9	3.60									
	19	1242	18.2	3.6									
	20	1302	23	3.6									
	21	1334	30.9	3.6									
	22	1444	29.9	3.6									
	23	1541	38.9	3.6									
	24	1551	37.2	0.2									
	25		33.6	0.2									
2/21	26	0715	-45.2	0.2									
	27	0900	-45.3	0.2									
	28	1135	-44.1	0.2									
	29	1440	-43.7	0.2									
	30	1600	-44.0	0.2									
2/22	31	0700	-40.6	0.2									
		0708	-25.2	2.0									

↓ flow rate to 0.2 ml/min. Empty effluent ± 700 mL N<sub>2</sub> 1750 psiN<sub>2</sub> = 1600 psi

↓ flow rate to 0.06 ml/min

↑ Flow to 3.60 ml/min

↓ Flow to 0.2 ml/min

↑ 2 ml/min

S. Morrison



Roll Flow

m PERIOD-02-14

	Time	ORP	3 ORP	4 RATE	5	6	7	8	9	10	11	12	13
2/22/00	1 0711	-20.0		2.0									
	2 0752	-11.5		2.0									
	3 0824	-3.0		2.0									
	4 Stopped experiment												
	5												
	6												
	7												
	8												
	9												
	10												
	11												
	12												
	13												
	14												
	15												
	16												
	17												
	18												
	19												
	20												
	21												
	22												
	23												
	24												
	25												
	26												
	27												
	28												
	29												
	30												
	31												

John Morrison



3-14-00

Examination of Polished Thin Sections Using  
Reflected Light (w/ Fukui)

There was no detectable difference between the unused sample (MPW-S-0) and the most altered (MPW-S-1) samples. The ZVI grains in MPW-S-1 still have the same shapes (curles, rods, etc.). There are no obvious alteration rims - although in both S-0 and S-1 there could be seen red internal reflections (beneath the epoxy?) along grain boundaries indicating red Fe-oxides.

The ZVI has numerous oval inclusion pits, also crescent shaped pits. It is pleochroic(?) i.e. changes color under X-nichols as stage rotated.

No sign of isotropic (magnetite) minerals.

I suspect that most of the alteration products (like magnetite - it was identified by XRD), were in the fine grained particulate (i.e. see EST article is probably good - they analysed fine particles as being oxide corrosion products).

Stan Morusin

3/17/00 met with Ralph Smith -  
to view digestates from samples 50 - 57.  
from the Monticello manuscript column.

Two digestion techniques were used. L-9  
which is a multiple acid (perchloric, nitric, HF).  
and microwave  $\text{HNO}_3$ .

A black residue was present in all tubes from  
both digestions. The microwave  $\text{HNO}_3$  liquid  
had a yellow color whereas the L-9 liquid  
was clear. The microwave  $\text{HNO}_3$  had a  
small amount of magnetic materials (large  
grains which appeared like original lathe-type  
morphology). The L-9 had no magnetic  
material. The non magnetic material in  
both was a finer grained black soot-like.

The residues will be saved so we can  
reanalyze (redigest) or X ray them.

We could be forming insoluble Fe oxides during  
the digestion.

Stan Morris



MPERT 01-02-17

①

MPW1		Collection							Cum					Pore				
	Date	Start	Finish	Vol	Time	Rate	Vol	Vol		10	11	12	13					
				(ml)	(min)	(ml/min)	(ml)	(1=13ml)										
1																		
2																		
start/waste	1/13/00	1130	1647	623 ✓	327	1.91	623	48										
MPW1-001E		1647	1745	100	58	1.72	723	56										
waste		1745	1800	—	15 *		—	—										
MPW1-001S		1800	1830	—	30		—	—										
waste		1830	910 <sup>1/4</sup>	1672 ✓	880	1.87	2395	184										
MAW1-002E	1/14/00	0910	1009	110	59	1.86	2505	193										
waste		1009	1022	—	13 *		—	—										
MPW1-002S		1022	1052	—	30		—	—										
waste	1/15/00	1052	0900 <sup>1/2</sup>	2365 ✓	1348	1.76	4870	375										
MPW1-003E		0900	0950	100	50	2.0	4970	382										
waste		0950	1000	—	10 *		—	—										
MPW1-003S		1000	1030	—	30		—	—										
waste		1030	0948 <sup>1/4</sup>	2833 ✓	1408	2.0	6378	491										
MPW1-004E	1/16/00	0948	1037 <sup>1/4</sup>	2833 <sup>1/4</sup>	49	2.0	6478	498										
waste		1037	0930 <sup>1/4</sup>	2764 ✓	1373	2.0	9242	711										
MPW1-005E	1/17/00	0930	1020	100	50	2.0	9342	719										
waste	1/18/00	1020	1030 <sup>1/2</sup>	2911 ✓	1450	2.0	12253	943										
waste	1/19/00	1030	0730 <sup>1/4</sup>	2510 ✓	1260	1.99	14763	1136										
MPW1-006E	1/19/00	0730	0820	100	50	2.0	14863	1143										
waste		0820	0765 <sup>1/4</sup>	5602 ✓	2805	2.0	20465	1574										
MPW1-007E	1/21/00	0705	0755	100	50	2.0	20565	1582										
waste		0755	0755 <sup>1/2</sup>	8554 ✓	4320	1.98	24885	1914										
MPW1-008E	1/24/00	0755	0845	100	50	2.0	24985	1922										
waste		0845	0900	—	15 *		—	—										
MPW1-004S		0900	0930	—	30		—	—										
waste		0930	1100 <sup>1/2</sup>	4653	2970	1.57	29638	2280										
MPW1-009E	1/26/00	1100	1200	100	60	1.67	29738	2288										
waste		0900	0900	3293	2700	1.22	33031	2541										
		1200	1128															

start flow to column. 1st outflow @ 1137

Note: <sup>interim</sup> Waste volume is accounted for when jug is weighed

interim waste is the vol between and E (effluent) and S (source) samples wh. they are taken consecutively.

Mark this with \*

weighed waste volume is marked ✓

switch to larger collection jug

switch to new source tank

John Morrison

start flow to column. 1st outflow @ 1137

Note: interim  
Waste volume is accounted for  
when jug is weighed  
interim waste is the vol between and  
E (effluent) and S (source) samples wh.  
they are taken consecutively.  
Mark this with \*

weighed waste volume is marked ✓

switch to larger collection jug

switch to new source tank





MPERT01-02-18

(2)

MPWI		Collection					Cum		Pac				
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Date	Start	Finish	Vol (ml)	Time (min)	Rate (ml/min)	Vol (ml)	Vol (1=13ml)					
1													
2													
MPWI-010E	1/28/00	0900	1020	100	80	1.25	33131	2549					
Waste		1020	0745 <sup>1/31</sup>	3610	4165	0.87	36741	2826					
MPWI-011E	1/31/00	0745	1023	100	158	0.63	36841	2834					
Waste		1023	1045	—	22	—	—	—					
MPWI-005S		1045	1200	—	75	—	—	—					
Waste	2/1/00	1200	0750	510	1272	0.42	37351	2873					
Stop	2/1/00	0750	0905	(Aerome flow									
Waste	2/2/00	0905	1345	resume flow	to column. Will collect sample later.								
MPWI-012E		1345		533	280	1.90	37884	2914					
↓		1345	1435	100	50	2.0	37984	2922					
Waste	2/4/00	1435	1045	5651	2650	2.1	43635	3357					
MPWI-013E	2/4/00	1045	1135	100	50	2.0	43735	3364					
Waste		1135	0800 <sup>2/7</sup>	1874	4105	1.92	51609	3970					
MPWI-014E	2/7	0800	0850	100	50	2.0	51709	3978					
Waste		0850	0900	—	10	—	—	—					
MPWI-006S	4/7	0900	0930 <sup>4/7</sup>	—	30	—	—	—					
Waste		0930	0730 <sup>4/7</sup>	5379	2770	1.94	57088	4391					
MPWI-015E	2/9	0730	0820	100	50	2.0	57188	4399					
Waste		0820	1005 <sup>2/11</sup>	5697	2985	1.91	62885	4837					
MPWI-016E	2/11	1005	1055	100	50	2.0	62985	4845					
Waste		1055	0805 <sup>2/14</sup>	7002	4150	1.83	70587	5430					
MPWI-017E		0805	0905	100	60	1.67	70687	5437					
Waste		0905	0925	—	20	—	—	—					
MPWI-007S		0925	0955	—	30	—	—	—					
Waste		0955											



MPERT01-02-19

MPWI	1 ORP	2 pH	3 alk	4 Cond	5 DO	6 U	7	8	9	10	11	12	13 Fp/mg/L
MPWI-001E <sup>1</sup>	+163	9.07	1020	1950		6.46							1.63
MPWI-001S <sup>2</sup>	+183	8.98	970	1917		<del>1997</del>	2003						<0.1
MPWI-002E	+191	9.04	1000	1947		2.99							1.66
MPWI-002S	+219	9.14	1005	1928		2076							<0.1
MPWI-003E <sup>5</sup>	+189	9.26	960	1956		3.04							1.01
MPWI-003S <sup>6</sup>	+208	9.22	1000	1933		1998							<0.1
MPWI-004E <sup>7</sup>	+175↓	9.31	1000	1953		4.34							0.76
MPWI-005E <sup>8</sup>	+148↓	9.35	970	1963	0.25	8.39							1.00
MPWI-006E <sup>9</sup>	+164	9.13	960	1942	0.29	20.722							0.46
MPWI-007E <sup>10</sup>	+189	9.24	930	1956	0.35	31.165							0.35
MPWI-008E <sup>11</sup>	+189	9.39	950	1985	0.31	<del>43.71</del>	68.10 87.70						<0.1
MPWI-004S <sup>12</sup>	+191	9.42	1010	1966	0.26	2034							<0.1
MPWI-009E <sup>13</sup>	+198	9.29	960	1938	0.40	25.795							0.32
MPWI-010E <sup>14</sup>	+200	9.23	980	1962	0.26	77.51							<0.1
MPWI-011E <sup>15</sup>	+188	9.46	910	1988	0.52	29.83							<0.1
MPWI-005S <sup>16</sup>	+174	9.45	990	1978	0.37	2088							<0.1
MPWI-012E <sup>17</sup>	+160.1	9.50	920	2010	0.40	60.66							<0.1
MPWI-013E <sup>18</sup>	+104.6	9.68	910	2020	0.16	416.10							<0.1
MPWI-014E <sup>19</sup>	+115.2	9.26	920	1956	0.19	<del>590.70</del>	688.3						<0.1
MPWI-006S <sup>20</sup>	+116.9	9.26	960	1948	0.43	2166							<0.1
MPWI-015E <sup>21</sup>	+124.4	9.41	1000	1980	0.15	379.9							<0.1
MPWI-016E <sup>22</sup>	+87.7	9.48	930	1989	0.14	1177.4							<0.1
MPWI-017E <sup>23</sup>	+113.1	9.13	970	1945	0.29	1054.9							<0.1
MPWI-007S <sup>24</sup>	+109.4	9.07	1020	1938	0.37	1984.4							<0.1
MPWI-018E <sup>25</sup>						129.4							
26													
27													
28													
29													
30													
31													

ORP continued to decrease +155 after 15 mins

Note: this is the only source sample out of Tank 2  
1st E sample from Tank 3

only S sample from Tank 3  
new ORP probe

1st E sample from Tank 4  
1st S sample from Tank 4

1st sample from Tank 5  
1st source sample from Tank 5  
end.

Sam Morris

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1/17/00	DO measurements											
2													
3	VSI	Probe Model 55 T											
4													
5		Chamber = 7.86 mg/L 7.20 after calibration											
6													
7		Na <sub>2</sub> SO <sub>3</sub> = 0.15 mg/L T = 21.6°C (pH = 9.39)											
8													
9		Hanging in SW = 0.12 mg/L											
10		TANK											
11		(Ar Purged)											
12													
13		Na <sub>2</sub> SO <sub>3</sub> = 0.10 mg/L (second measurement)											
14													
15		ORP of Na <sub>2</sub> SO <sub>3</sub> = at 6:28 205 mV											
16		6:29 202											
17		6:32 197											
18		6:35 192											
19													
20													
21													
22													
23													
24													
25													
26													
27													
28													
29													
30													
31													





**Appendix C**  
**Data Summary**

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